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ILLINOIS UNIV AT URBANA-CHAMPAIGN DEPT OF CHEMISTRY

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DETECTION AND TRAPPING OF A CHEMILUMINESCENT ORTHO-XYLYLENE PER--ETC(U)

OCT 77 J P SMITH, G B SCHUSTER

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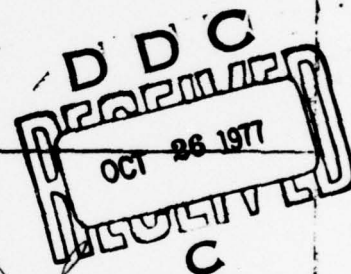
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20. ABSTRACT (Continue on reverse side if necessary and identify by block number)

Thermolysis of pyranone exdoperoxide (1) (prepared by singlet oxygenation of 1,4-diphenyl-2-benzopyran-3-one) in benzene solution leads to o-xylylene peroxide (2). Peroxide (2) is trapped in a Diels-Alder reaction with maleic anhydride to yield adduct (6). It was observed that the chemiluminescence that resulted from the thermal reaction of peroxide (2) occurred by two distinct paths. The first occurred in the absence of easily oxidized aromatic hydrocarbons and was the result of the unimolecular rearrangement of (2) to



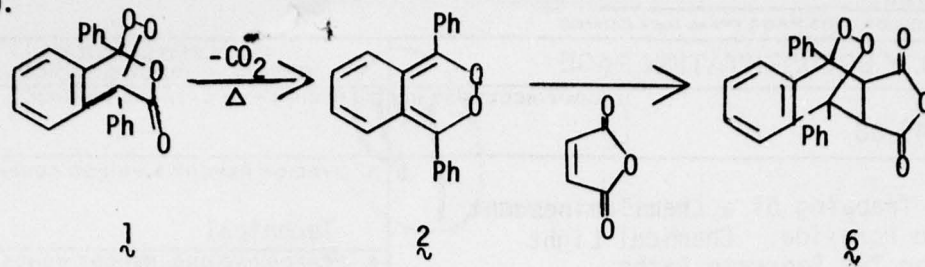
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electronically excited o-dibenzoylbenzene (4). In this case chemiluminescence was detected by energy transfer from excited (4) to suitable acceptors. The second occurred when any one of several easily oxidized aromatic hydrocarbons was included in the reaction solution. In this case light generation is apparently the result of chemically initiated electron exchange luminescence.

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6 Detection and Trapping of a Chemiluminescent Ortho-Xylylene Peroxide.
Chemical Light Formation Along two Separate Paths.

by

10 Jimmie P. Smith and Gary B. Schuster

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Detection and Trapping of a Chemiluminescent Ortho-Xylylene Peroxide:
Chemical Light Formation Along Two Separate Paths

By Jimmie P. Smith and Gary B. Schuster*¹²

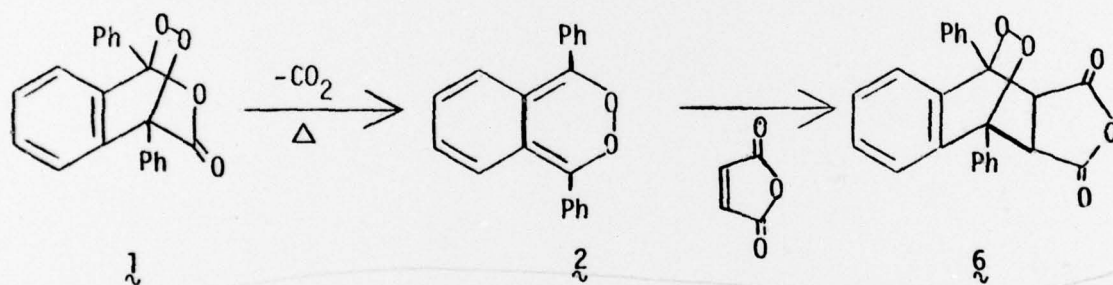
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Detection and Trapping of a Chemiluminescent Ortho-Xylylene Peroxide;

Chemical Light Formation Along Two Separate Paths.

By Jimmie P. Smith and Gary B. Schuster*¹²

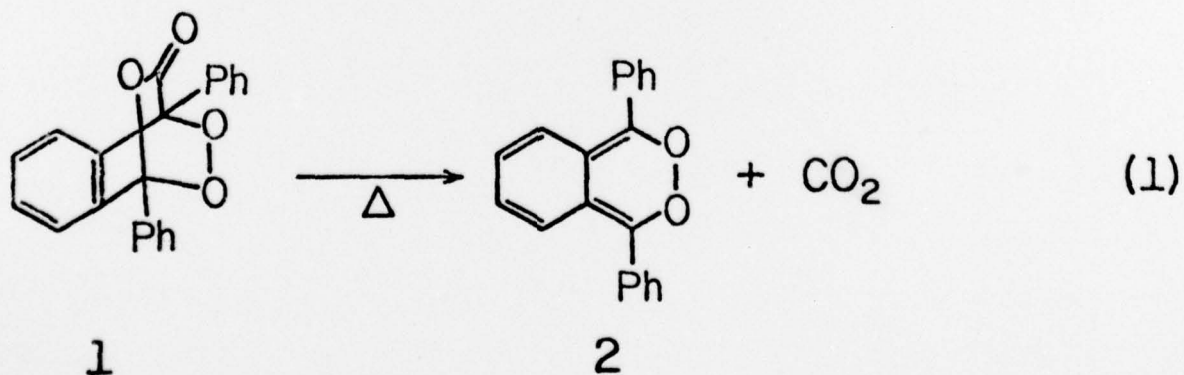
Abstract: Thermolysis of pyranone endoperoxide (1) (prepared by singlet oxygenation of 1,4-diphenyl-2-benzopyran-3-one) in benzene solution leads to o-xylylene peroxide (2). Peroxide (2) is trapped in a Diels-Alder reaction with maleic anhydride to yield adduct (6).



It was observed that the chemiluminescence that resulted from the thermal reaction of peroxide (2) occurred by two distinct paths. The first occurred in the absence of easily oxidized aromatic hydrocarbons and was the result of the unimolecular rearrangement of (2) to electronically excited o-dibenzoylbenzene (4). In this case chemiluminescence was detected by energy transfer from excited (4) to suitable acceptors. The second occurred when any one of several easily oxidized aromatic hydrocarbons was included in the reaction solution. In this case light generation is apparently the result of chemically initiated electron exchange luminescence.

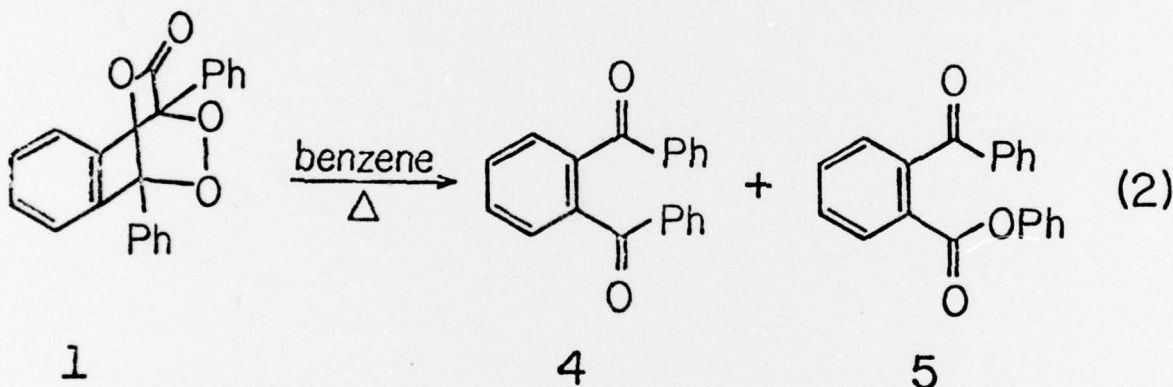
Sir:

The thermal chemistry of organic molecules containing an oxygen-oxygen bond is usually dominated by reactions involving homolytic or heterolytic cleavage of the peroxide linkage.¹ In this report we would like to describe our observation of a novel retro cycloaddition pathway for thermolysis of pyranone endoperoxide **1** to generate o-xylylene peroxide **2**. This is the first reported characterization of this interesting ring system. We have also found that thermolysis of the o-xylylene peroxide is chemiluminescent. There are two separate reaction pathways leading to light generation for this molecule. In the absence of an easily oxidized substrate, o-xylylene peroxide **2** rearranges to generate electronically excited o-dibenzoylbenzene (**4**). In this case chemiluminescence is detected following energy transfer to a suitable emitting energy acceptor, such as biacetyl. The second chemiluminescent path occurs in the presence of any one of several easily oxidized aromatic hydrocarbons. In this case, o-xylylene peroxide **2** undergoes a bimolecular reaction resulting in the generation of the fluorescent singlet state of the aromatic hydrocarbon. The mechanism for light formation under these conditions is apparently that which we have recently identified as chemically initiated electron exchange luminescence.²

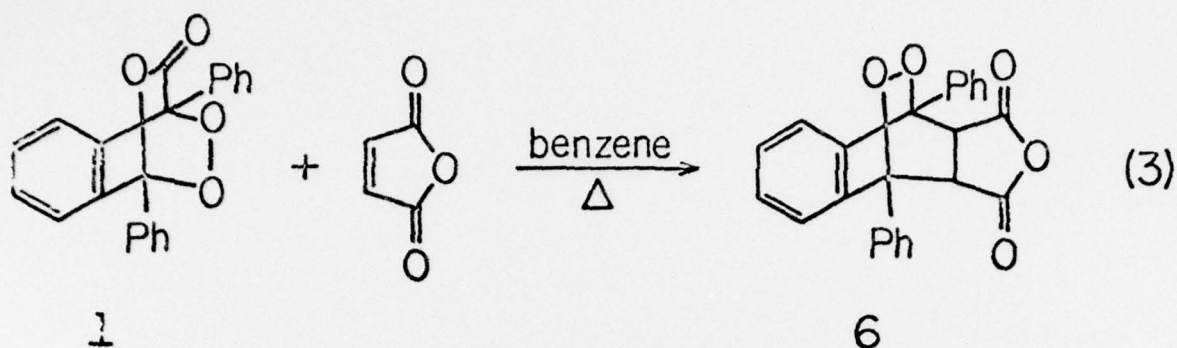


Photooxidation of 1,4-diphenyl-2-benzopyran-3-one³ (**3**) in acetone at 0° with methylene blue as sensitizer results in the isolation of endoperoxide **1** as a white crystalline solid (M.P. 105°) in 60% yield.⁴ This compound is stable in crystalline form at room temperature. Peroxide **1**, however, is completely decomposed when subjected to refluxing benzene for 6 h. The products isolated from this reaction are o-dibenzoylbenzene (**4**) and phenyl-(o-benzoyl)-benzoate (**5**) in 85% and 5% yield respectively.⁵

Importantly, it is observed that when this reaction is carried out in rigorously deoxygenated solvent, a deep yellow color develops in the solution as the reaction progresses. The yellow intermediate shows a maximum in its absorption spectrum at 410 nm that tails out to 430 nm.



Also, this intermediate is rapidly decolorized by the addition of oxygen to the reaction solution. When the thermolysis of **1** is carried out in the presence of excess maleic anhydride, the yellow intermediate is not observed, the yield of o-dibenzoylbenzene is much reduced, and the yield of ester **5** is essentially unchanged.⁶ The major product of the reaction under these conditions is identified as the Diels-Alder adduct (**6**) of maleic anhydride and ester **5**. Adduct (**6**) is isolated as a crystalline solid in 70% yield.⁷ These observations are entirely consistent



with the formation of *o*-xylylene peroxide **2** by retro-Diels-Alder loss of CO₂ as the major reaction path for **1**. Compounds containing the *o*-xylylene moiety have recently been characterized in the absence of oxygen under relatively mild conditions.⁸ The absorption spectra of these related compounds and the observed chemistry are similar to that which we have found for the intermediate in the thermal reaction of **1**.

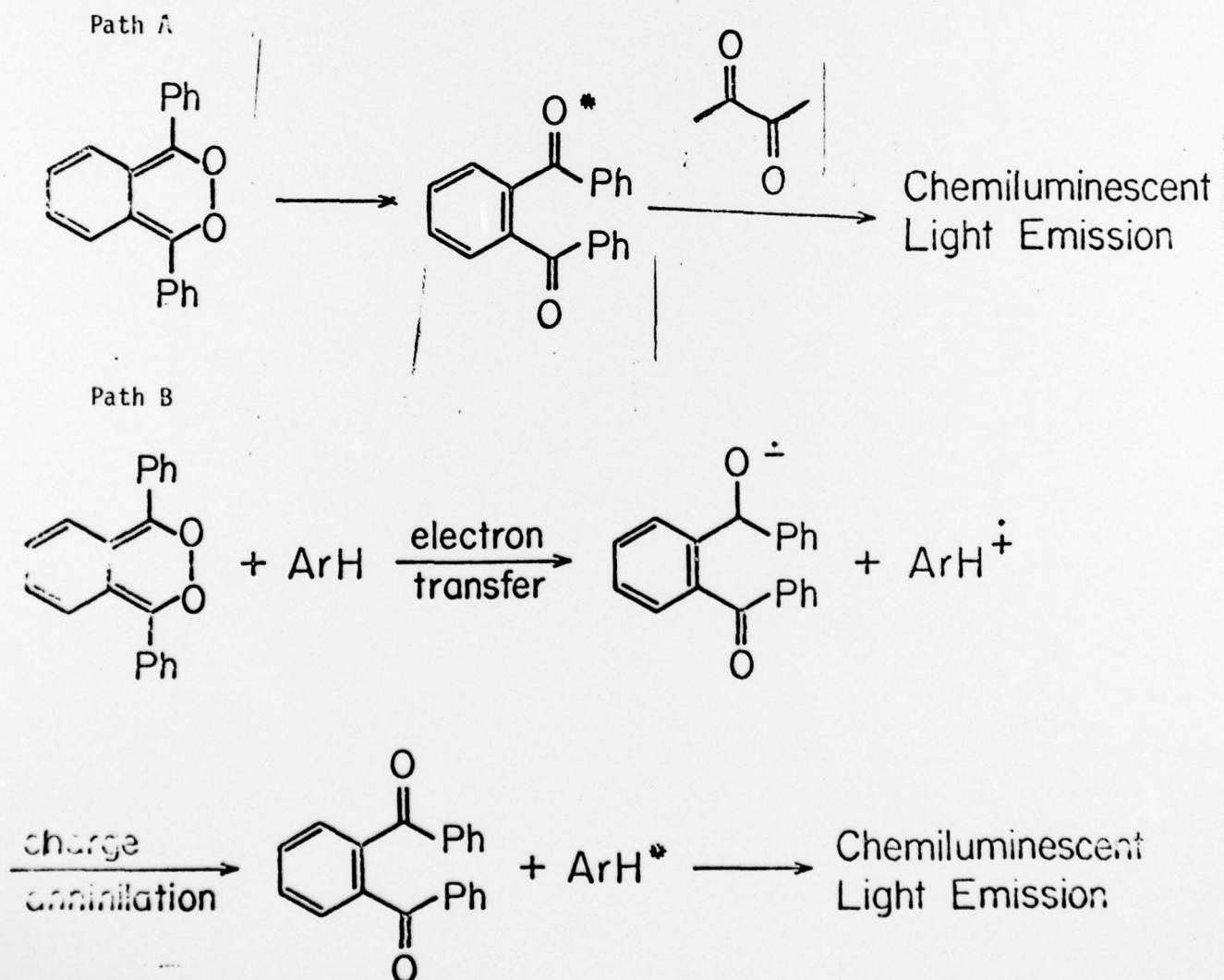
Apart from the exciting chemistry involved in the formation, reactions, and properties of **2**, this *o*-xylylene peroxide represents an example of a potentially important new class of chemiluminescent reagents. Thermolysis of **1** in a photon counting apparatus at 92° does not produce a detectable luminescence. This result was not unexpected since only inefficient emission is expected from the excited states of *o*-dibenzoylbenzene under these conditions. However, addition of biacetyl to the reaction solution resulted in easily detected phosphorescence from triplet excited biacetyl.⁹ Moreover, it is also observed that addition of rubrene, perylene or any one of several easily oxidized aromatic hydrocarbons results in readily detected luminescence. The luminescence in this case corresponds to fluorescence from the added aromatic hydrocarbon singlet excited state. The intensity of the chemiluminescence is directly proportional to the concentration of endoperoxide **1** and decays following a first order kinetic law.

Our observation of the chemiluminescence from 1 implicates the o-xylylene peroxide 2 as the chemiluminescent precursor.¹⁰ In particular, addition of maleic anhydride to a chemiluminescing solution of 1 and perylene quenches the chemiluminescence without affecting the rate of consumption of endoperoxide 1 .¹¹ The energy stored in o-xylylene peroxide 2 must ultimately appear as the energy of electronic excitation on the added emitter. We have found that there are two kinetically and spectroscopically distinguishable mechanisms operating to transform the potential energy of o-xylylene peroxide 2 to an excited state of the emitter. In the first, exemplified for biacetyl, endoperoxide 1 loses CO_2 to form 3 , which in a subsequent surprisingly slow unimolecular rearrangement forms electronically excited o-dibenzoylbenzene (4). Energy transfer from excited ketone 4 to biacetyl results in the formation of the observed emitting triplet state of biacetyl. It should be noted that the concerted rearrangement of peroxide 2 to ketone 4 is a formally forbidden process which would result in generation of a high energy doubly excited state. Consistent with this mechanistic interpretation we observe classical consecutive reaction kinetics, shown in figure 1, for the build-up and decay of chemiluminescence emission intensity under these conditions. This mechanism for light generation is shown as path A in Scheme 1.

The second route leading to light emission occurs in the presence of any one of several easily oxidized aromatic hydrocarbons (ArH) and is an example of the general excitation mechanism we have recently identified as chemically initiated electron exchange luminescence. The initial interaction between o-xylylene peroxide 2 and ArH in this case is an electron transfer from ArH to the peroxide. Subsequent ring opening of the reduced peroxide followed by annihilation of the resulting radical ions generates the observed products, o-dibenzoylbenzene and electronically excited aromatic

hydrocarbon as is shown in path B of Scheme 1. Evidence that this path is operating comes from the observation that the singlet excited state of ArH is efficiently formed under conditions where energy transfer from singlet 4 is highly improbable. Also, the efficiency of light production is proportional to the one electron oxidation potential of ArH indicating an electron transfer as a key step in the excitation sequence. Finally, the kinetic behavior of the light intensity in the presence of ArH, shown in figure 1, indicates that the rate of reaction of the intermediate σ -xylylene peroxide 2 has been increased by the addition of ArH so that the formation of 2 from endoperoxide 1 is now rate determining.

Scheme 1



In summary, we have observed a novel thermal reaction of pyranone endoperoxide 1 to form the unique o-xylylene peroxide 2. This peroxide represents one of the few known or postulated vinyl peroxides. In addition, o-xylylene peroxide 2 reacts along two distinct paths to produce chemiluminescent emission. These observations may be extrapolated to the much studied isoelectronic luminol system in which intramolecular electron exchange is possible. We are continuing to investigate the interesting and novel chemical and chemiluminescent reactions of endoperoxide 1 and related systems.

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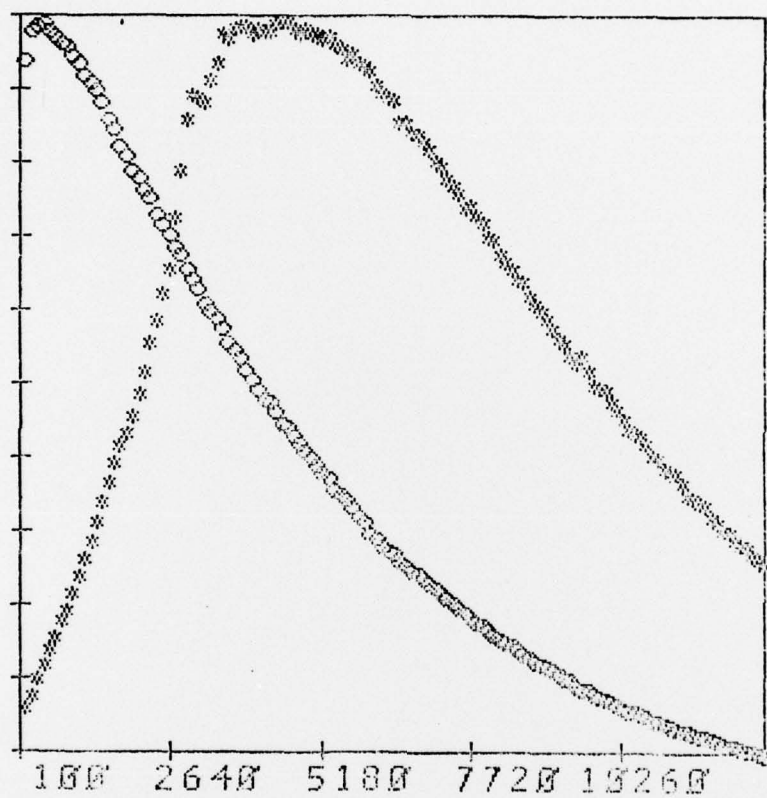
References and Notes

1. For leading references see, Organic Peroxides, D. Swern, ed., Wiley Interscience, 1970.
2. J. Y. Koo and G. B. Schuster, J. Am. Chem. Soc., 99, 6107 (1977).
3. J. M. Holland and D. W. Jones, J. Chem. Soc. (C), 530 (1970).
4. The endoperoxide was characterized as follows: Ir (CHCl₃) 2950, 1785, 1525, 1460, 1330 cm⁻¹. ¹H NMR (CDCl₃, internal TMS) δ 6.8-7.0 (m, 2H), 7.2-7.9 (m, 12H); ¹³C NMR (CDCl₃, internal TMS) δ 166, 136, 130.8, 130.2, 129.6, 129.3, 128.8, 128.2. Analysis; Calcd. for C₂₁H₁₄O₄; C, 76.36; H, 4.24; Found; C, 76.36; H, 4.27. Molecular Weight (Osmometry) required 330; found 328 ± 4. Active oxygen content; 87 ± 10% of theoretical.
5. These compounds were identified by comparison with authentic samples. The o-dibenzoylbenzene was prepared according to: J. R. Jenkins, J. Org. Chem., 25, 269 (1960) and the phenyl-(o-benzoyl)-benzoate according to: J. J. Bieke and R. D. Swisler, J. Am. Chem. Soc., 56, 902 (1934).
6. This observation is consistent with formation of 2 and 5 along parallel paths from 1.
7. The adduct was characterized as follows: Ir (CHCl₃) 2980, 1870, 1690, 1600, 1490 cm⁻¹. ¹H NMR (CDCl₃, internal TMS) δ 7.0-7.85 (m, 14H), δ 4.1 (s, 2H). Analysis; Calcd for C₂₄H₁₆O₅; C, 74.99; H, 4.20; Found C, 74.65; H, 4.28. Molecular Weight (Osmometry) required 384; found 381 ± 5. Active oxygen content 94.4 ± 6% of theoretical. The stereochemistry of 6 is not yet known.
8. Leading references: a) K. L. Tseng and J. Michl, J. Am. Chem. Soc., 99, 4840 (1977); b) W. R. Dolbier, Jr., K. Matsui, J. Michl and D. U. Horak, J. Am. Chem. Soc., 99, 3876 (1977); c) E. Chacko,

- J. Bornstein and D. J. Sardella, Tetrahedron Lett., 1095 (1977);
d) R. D. Miller, J. Kolc, and J. Michl, J. Am. Chem. Soc., 98, 8510 (1976); e) D. S. Weiss, J. Am. Chem. Soc., 97, 2550 (1975).
9. The triplet and singlet energy of o-dibenzoylbenzene is above that of biacetyl; G. S. Hammond, J. Saltiel, A. A. Lamola, N. J. Turro, J. S. Bradshaw, D. O. Cowan, R. C. Counsell, V. Vogt, and C. Dalton, J. Am. Chem. Soc., 86, 3197 (1964).
10. In a recent review Michl has suggested, based on theoretical considerations, that an o-xylylene peroxide is the key chemiluminescent intermediate in the light forming reaction of luminol: J. Michl, Photochemistry and Photobiology, 25, 141 (1977).
11. Typical conditions. $[I] = 5 \times 10^{-4} M$, $[perylene] = 2 \times 10^{-4} M$, $[Maleic Anhydride] = 1 \times 10^{-3} M$ in benzene at 92° . Maleic anhydride will not significantly quench perylene singlets under these conditions.
12. Fellow of the Alfred P. Sloan Foundation 1977-1979.

Decay of Chemiluminescence from endoperoxide I_2 in benzene solution at 92° . The open circles are for solutions containing perylene, the stars are for biacetyl containing solutions.

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